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COMMERCIAL SOLVENTS CORPORATION

TERRE HAUTE, INDIANA

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August 11, 1952
Copy No. 15

Report No. Q-3
(Quarterly Summary)

SUBJECT: ONR Nitropolymer Research

CONTRACT: Nonr-397(00)

PERIOD COVERED: May 1, 1952 to July 31, 1952

SUBMITTED BY: John T. Minor

APPROVED BY: Jerome Martin
Jerome Martin
Director of Research

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SECURITY INFORMATION

COMMERCIAL SOLVENTS CORP. Report No. Q-3

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CONTRACT FULFILLMENT

This quarterly report is submitted in partial fulfillment of Contract Nonr-397(00).

COMMERCIAL SOLVENTS CORP. Report No. Q-3

I. SUMMARY

A. This quarterly summary report is the third under Contract Nonr-397(00) and covers the period from May 1, 1952 to July 31, 1952. The object of this contract is as follows: Shall conduct research in the synthesis of polynitro compounds to include, but not necessarily be limited to, a review of the chemistry and the processes of preparation of the more useful products of research from the nitropolymer program and investigate the application of processes not now employed in the preparation.

B. The more important results and conclusions of the work reported are presented below:

1. By the use of the oxidative-nitration reaction, 1065 lbs. of 2,2-dinitropropane have been produced in the pilot plant.

2. The Scheibel type extraction column was used for the extraction of 2-nitro-1,3-propanediol with butanol. One packed section was equivalent to one stage.

3. The 2-nitro-1,3-propanediol butanol extract was catalytically reduced to obtain a 21% yield of 2-amino-1,3-propanediol.

4. Methyl 4,4-dinitroheptanedioate was prepared according to the procedure of Aerojet, but only a 24% overall yield could be obtained as compared to a reported 36.5% overall yield.

5. A Wurtz reaction was attempted using 1-chloro-2-nitroethane in an anhydrous ether solvent. No reaction could be detected after seven days.

6. No 1,1-dinitro-2-butanol could be obtained by the application of the oxidative-nitration technique to 1-nitro-2-butanol.

II. TECHNICAL PROGRESS

A. INTRODUCTION

The present program is directed toward the industrial development of nitropolymer starting materials and nitropolymer intermediates.

With process comparison the main object and the production of 2,2-dinitropropane as a direct result, 2000 lbs. of dinitropropane are to be produced by two methods. The preparation of 1000 lbs. of dinitropropane from 2-nitropropane by the oxidative-nitration reaction has been completed and some conclusions drawn. This has required the major portion of the quarter's time. The preparation of the remaining 1000 lbs. by the liquid phase nitration of propane has begun.

B. PILOT PLANT PRODUCTION OF 2,2-DINITROPROPANE

By the use of the oxidative-nitration reaction of Shechter and Kaplan, 1065 lbs. of 2,2-dinitropropane (DNP) were made in 53 separate batches. These runs were made in the pilot plant with unskilled operators on a three shift basis; therefore, supervision was not continuous. The first seven batches are eliminated from our treatment because of instructional errors which resulted in the use of excess silver nitrate. Batch 21 was omitted from the treatment also as a clogged valve caused mechanical loss of silver. The limits to the arithmetic means are mean deviations.

Yield of steam distilled 2,2-dinitropropane - 21.1±1.0 lbs. per batch, or 89.7±4.7%.

Silver nitrate recovery - 98.6±1.0%.

Fifty-four per cent of the runs had recoveries better than the average and in themselves had a mean of 99.5%.

The time per batch averaged 11.0 hrs. Two batches were run concurrently, so that the silver nitrate recovery was handled for one batch as the other batch was being run. A typical run would be as follows:

The wet silver cake from the previous run which averages 67.4±3.9 lbs. is placed in a stainless steel vessel and concentrated nitric acid equivalent to 29.7 lbs (0.472 lb.-mole) of pure acid is added in portions. After the reaction has subsided, 40 lbs. of water are added and the solution is agitated and heated in a water bath to 80°C. When the silver is all dissolved, cool, bring to 200 lbs. of total solution and analyze for silver nitrate; average analysis is 59.2 lbs. (98.6±1.0%). From the analysis add silver nitrate (0.8±0.5 lb.) to bring the total weight of silver nitrate in solution to 60.0 lbs. (0.352 lb.-mole) and adjust the pH at 5.5 to 6.0 with sodium hydroxide.

To this silver nitrate solution at 15 to 20°C. is added as rapidly as possible and with vigorous agitation the following solution: 220 lbs. of water, 7.7 lbs. (0.183 lb.-mole) of 95% flake caustic, 16.0 lbs. (0.179 lb.-mole) of 2-nitropropane, and 13.2 lbs. (0.183 lb.-mole) of 95% sodium nitrite. By the use of cooling water the reaction kettle is held to 25°C.

After stirring the reaction for ½ hr., the slurry is pumped to a kettle where it is steam distilled to obtain 21.1±1.0 lbs. (0.158 lb.-mole; 89.7±4.7%) of 2,2-dinitropropane. The steam distillate water is used as make-up for subsequent reaction batches. The material remaining in the kettle is filtered and the silver cake reconverted to silver nitrate. The filtrate is analyzed for silver and if negative, discarded. The freezing point of the solid product is 50.1±1.0°C.

The estimated cost for material and labor for dinitropropane prepared in this quantity based on the mean yield and loss is:

Silver nitrate make-up	$6.90
Other materials	6.94
Labor	46.86
Total for 21.1 lbs.	60.70
Cost per pound	$2.88

If the silver nitrate loss could be cut in half, or to a 99.3% recovery, and the same labor used to prepare batches on a 2 lb.-mole scale, requiring a 600-gal. reactor, the cost of material and labor would be cut to $0.69 per lb.

C. THE USE OF THE SCHIEBEL COLUMN FOR EXTRACTING 2-NITRO-1,3-PROPANEDIOL

As suggested previously[1] there is need for an efficient extraction column in the 2-nitro-1,3-propanediol process. A Schiebel-type column, 2 in. x 32 in., containing 7 packed sections and 6 impellers was tested in extracting an 8 g.-mole run with butanol. When the rate of feed was 53 ml. per min. and the butanol feed rate was 42 ml. per min., 20% of the NPD was not extracted. Thus, a larger ratio of extractant must be used and/or more sections added to the column.

One-half of the butanol extract was concentrated and reduced with hydrogen over Raney nickel catalyst. A 21% yield of 2-amino-1,3-propanediol was obtained based on the starting nitromethane.

D. THE PREPARATION OF METHYL 4,4-DINITROHEPTANEDIOATE

The procedure of Aerojet[2] was used to prepare methyl 4,4-dinitroheptanedioate from nitromethane and methyl acrylate. The 15 g.-mole procedure is reported to give 36.5% overall yield. In three runs on a 1.5 g.-mole basis, only a 24% yield of solid ester could be obtained.

E. ATTEMPTED WURTZ REACTION WITH 1-CHLORO-2-NITROETHANE.

A Wurtz reaction was attempted with 1-chloro-2-nitroethane in anhydrous ethyl ether. No reaction had ensued by the seventh day. An attempt was made to react the 1-chloro-2-nitroethane and sodium in the absence of solvent. A vigorous reaction occurred, resulting in charred material.

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1. C.S.C. Report No. Q-2, p. 2.

2. Aerojet Report No. 468, Appendix B.

F. ATTEMPTED PREPARATION OF 1,1-DINITRO-2-BUTANOL

In attempts to prepare 1,1-dinitro-2-butanol from 1-nitro-2-butanol by oxidative-nitration, no product was obtained. When the starting materials, nitromethane and propanal, were used, only nitrobutanol could be isolated.

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